© 1985 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 58, 2648—2651 (1985) [Vol. 58, No. 9

A Nuclear Magnetic Resonance Study of the Exchange Reaction of Dimethyl Sulfoxide in Pentakis(dimethyl sulfoxide)oxovanadium(IV) Ions

Kiyoshi KAYA, Yasuhisa IKEDA, and Hiroshi FUKUTOMI*
Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology,
O-okayama, Meguro-ku, Tokyo 152
(Received March 19, 1985)

The dmso exchange reaction in $[VO(dmso)_5]^{2+}$ has been studied in the mixture of CD_3NO_2 and DMSO by means of ^1H NMR. The exchange rate is independent of the free DMSO concentration and the kinetic parameters are as follows: $k_{ex}(25\,°C)=1.76\times10^3\ s^{-1}$, $\Delta H^{\neq}=60.1\pm4.3\ kJ\ mol^{-1}$, and $\Delta S^{\neq}=18.5\pm12.9\ JK^{-1}\ mol^{-1}$.

Ligand-exchange reactions in several oxovanadium (IV) complexes have been studied by using the NMR line-broadening method,[1–4] but the mechanisms for these reactions have not been proposed in detail. On the other hand, Lincoln[5] has shown that the plot of $\Delta H^{\neq}$ *vs.* $\Delta S^{\neq}$ for ligand-exchange reactions in oxovanadium(IV) complexes is linear and consistent with that for the ligand-exchange reactions in various uranyl(VI) complexes in which the reactions proceed dissociatively. Such an isokinetic relationship suggests that the reactivity of oxovanadium(IV) ions is very similar to that of uranyl(VI) ions, and that the ligand-exchange reactions in oxovanadium(IV) complexes seem to proceed dissociatively. However, the associative mechanism has been proposed for some complex-formation reactions in oxovanadium(IV) ions.[6–8] From this point of view, further studies for the ligand-exchange reactions in oxovanadium(IV) complexes are necessary to understand the mechanisms in detail. This paper reports the exchange of dmso (dimethyl sulfoxide) in the $[VO(dmso)_5]^{2+}$ ion. This reaction has already been studied by Angerman and Jordan with the NMR line-broadening method,[3] but no accurate kinetic parameters have been determined, because the slow exchange region, where the relaxation time is controlled by the chemical exchange rate,[9] was not observed in the temperature range above the freezing point of DMSO. In the present study, CD_3NO_2 was used as a diluent in order to extend the lower limit of temperature range. As a result, it became possible to observe the slow exchange region and to determine the kinetic parameters.

Experimental

The $[VO(dmso)_5](ClO_4)_2$ complex was synthesized by the same method as described in a previous paper.[10] Anal. Calcd for $[VO(dmso)_5](ClO_4)_2$: C, 18.30; H, 4.61; S, 24.42. Found: C, 18.28; H, 4.56; S, 24.38. Dimethyl sulfoxide (Wako Pure Chemical Ind. Ltd.) was distilled *in vacuo*, followed by distillation with 3A molecular sieves (Wako), and stored over 3A molecular sieves. Nitromethane-d_3 (CD_3NO_2, Merck 99%), which was used as a diluent and an NMR lock reagent, was dried over 3A molecular sieves. The UV and visible spectra of the $[VO(dmso)_5]^{2+}$ ion in DMSO and in the mixture of CD_3NO_2 and DMSO were measured on a Shimadzu UV-210A double-beam spectrophotometer. Sample solutions for NMR measurements were prepared by weighing $[VO(dmso)_5](ClO_4)_2$, DMSO, and CD_3NO_2 in a 1 cm^3 volumetric flask and were placed in NMR sample tubes and sealed under vacuum. All samples were prepared in a glove-box filled with dried nitrogen. ^1H NMR spectra of bulk DMSO were measured at 100 MHz on a JEOL JNM-FX 100 FT-NMR spectrometer equipped with a JNM-VT-3B temperature controller. Typical spectral settings are as follows: data points, 8K; spectral width, 1000 Hz; pulse width, 14 μs; pulse delay time, 2.5 s; number of scan, 4.

Results and Discussion

The absorption spectrum of the $[VO(dmso)_5]^{2+}$ ion in DMSO was measured, and the two absorption bands at 820 and 690 nm were assigned to the $^2B_2\rightarrow{}^2E(I)$ and $^2B_2\rightarrow{}^2B_1$ (10 Dq) transitions, respectively, from the molecular orbital diagram of Ballhausen and Gray.[11] Based on this assignment, Dq is calculated to be 1450 cm^{-1} and is consistent with that obtained by Angerman and Jordan.[3] The absorption spectrum of the $[VO(dmso)_5]^{2+}$ ion in the mixture of CD_3NO_2 and DMSO was compatible with that in DMSO. This fact indicates that the $[VO(dmso)_5]^{2+}$ ion has the same solvation structure in both solvents, DMSO and the mixture of CD_3NO_2 and DMSO.

On the basis of the spectrophotometric results, the dmso exchange in the $[VO(dmso)_5]^{2+}$ ion was measured in the mixture of CD_3NO_2 and DMSO by using the NMR line-broadening method. The line-width and chemical shift of the methyl proton signal of bulk DMSO in the presence and absence of the $[VO(dmso)_5]^{2+}$ ion were measured by varying temperature from −45 to 70 °C. In this temperature range, the line-width of methyl proton signal of DMSO changed with temperature, while no change was observed in chemical shift of the corresponding signal. In this case, the transverse relaxation time (T_2) is expressed as follows:[9]

$$\frac{1}{T_2}=\frac{1-p_m}{p_m}\left(\frac{1}{T_{2p}}-\frac{1}{T_{2a}}\right)=\frac{1}{T_{2m}+\tau_m}+\frac{1}{T_{2o}}, \qquad (1)$$

where T_{2p} and T_{2a} are the transverse relaxation times of nuclei in the bulk solvent in the presence and absence of the paramagnetic metal ion, respectively, and are related with the full line-width ($\Delta\nu$) at half-height as $1/T_{2p}=\pi\Delta\nu_p$ and $1/T_{2a}=\pi\Delta\nu_a$, p_m is the ratio of the concentration of solvent bound to the paramagnetic metal ion to the concentration of free solvent, τ_m is the solvent exchange lifetime, T_{2m} is the transverse relaxation time of the coordinated solvent, and T_{2o} is the relaxation time of solvent outside the first-coordination sphere of the paramagnetic metal ion. The ralationship between τ_m and the first-order rate constant (k_{ex}) with temperature is as follows:

$$1/\tau_m = k_{ex} = (kT/h)\exp(-\Delta H^{*}/RT)\exp(\Delta S^{*}/R), \quad (2)$$

and the temperature dependence of T_{2m} and T_{2o} is assumed to be given by Eqs. 3 and 4, respectively.[12]

$$\frac{1}{T_{2m}} = C_m \exp\left(\frac{E_m}{RT}\right) \quad (3)$$

$$\frac{1}{T_{2o}} = C_o \exp\left(\frac{E_o}{RT}\right) \quad (4)$$

The values of T_2 were calculated based on the equatorial coordination number of four and from the assumption that the dmso exchange in the axial site is very faster than that in the equatorial site,[2,3] and hence only the dmso exchange in the equatorial site contributes to the line-broadening in the present temperature range. Figure 1 shows the typical plot of $\ln(1/T_2)$ *vs.* the reciprocal temperature. This figure indicates that T_2 is controlled by T_{2m}, τ_m, and T_{2o} successively as the temperature decreases, and that the above assumption is reasonable. If the dmso exchange in the axial site is not much faster than that in the equatorial site in the present temperature range, the value of $1/T_2$ should decrease again in the low temperature range as observed in the dmf (*N,N*-dimethylformamide) exchange in $[\mathrm{VO(dmf)_5}]^{2+}$ ions.[4] Kinetic parameters were determined by a nonlinear least-squares fit of $1/T_2$ data to the equation obtained by substitution of Eqs. 2, 3, and 4 into Eq. 1. Kinetic parameters for solutions with various compositions were determined by the same manner and are listed in Table 1. The table shows that the exchange rate is independent of the concentration of DMSO and the $\Delta S^{\neq}$ values are positive. These results suggest that the dmso exchange in the equatorial site of the $[\mathrm{VO(dmso)_5}]^{2+}$ ion proceeds through either the D or $\mathrm{I_d}$ mechanism. On the other hand, the activation volume ($\Delta V^{\neq}$) for the dmso exchange reaction was determined to be $-5.3\pm0.4\ \mathrm{cm^3\,mol^{-1}}$ in our recent study,[10] and suggested that the reaction proceeded associatively. Since the $\Delta S^{\neq}$ value is in conflict with the $\Delta V^{\neq}$ value, it is difficult to infer the mechanism of dmso exchange reaction. However, the A mechanism is excluded because the rate of dmso exchange is independent of [DMSO]. Furthermore, the D mechanism also seems to be unlikely from the following reasons. It was proposed that the solvent exchange reactions proceeding through the D mechanism have the positive $\Delta V^{\neq}$ value, because no net change occurs before and after the exchange reaction, so that negligible solvational change is expected and the observed $\Delta V^{\neq}$ value reflects the intrinsic volume change.[13,14] In addition, it was suggested that the

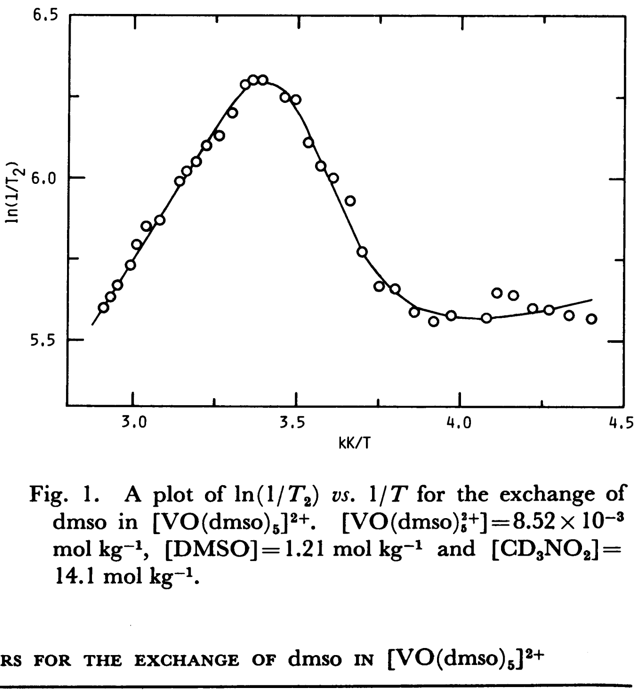

Fig. 1. A plot of $\ln(1/T_2)$ *vs.* $1/T$ for the exchange of dmso in $[\mathrm{VO(dmso)_5}]^{2+}$. $[\mathrm{VO(dmso)_5^{2+}}]=8.52\times10^{-3}$ mol kg^{-1}, [DMSO]=1.21 mol kg^{-1} and $[\mathrm{CD_3NO_2}]=$ 14.1 mol kg^{-1}.

TABLE 1. SOLUTION COMPOSITIONS AND KINETIC PARAMETERS FOR THE EXCHANGE OF dmso IN $[\mathrm{VO(dmso)_5}]^{2+}$

Solution	$[\mathrm{VO(dmso)_5^{2+}}]$ / 10^{-3} mol kg^{-1}	[DMSO] / mol kg^{-1}	$[\mathrm{CD_3NO_2}]$ / mol kg^{-1}	k_{ex}(25 °C) / 10^3 s^{-1}	ΔH^{*} / kJ mol^{-1}	ΔS^{*} / J K^{-1} mol^{-1}	S.D.[a]
i	10.0	0.314	15.9	1.51	66.5	39.1	0.05
ii	9.86	0.557	15.6	1.32	61.5	21.2	0.05
iii	9.71	0.716	15.4	2.51	56.9	11.1	0.07
iv	8.52	1.21	14.1	1.32	61.5	21.2	0.04
v	9.74	1.62	14.2	2.13	54.0	0.0	0.06

a) Standard deviation (S.D.) of nonlinear least-squares fit of $1/T_2$ data to the equation obtained by substitution of Eqs. 2, 3, and 4 into Eq. 1. S.D.$=\sqrt{\Sigma\{(Y_e-Y_c)^2/(n-1)\}}$, where Y_e and Y_c are the experimental and calculated values of $1/T_2$, respectively, and n is the number of experimental points.

$\Delta S^{\neq}$ value does not necessarily reflect the activated state owing to the contribution of the solvent rearrangement around the metal complexes, especially in mixed solvents.[15]

In the I mechanism, the exchange process in the equatorial site is expressed as follows:

$$[\mathrm{VO(dmso)_5}]^{2+} + \mathrm{DMSO}^* \overset{K_{os}}{\rightleftharpoons} [\mathrm{VO(dmso)_4(dmso)_{ax}}]^{2+}\cdots\mathrm{DMSO}^*$$

$$\xrightarrow[\text{slow}]{k_\mathrm{I}} [\mathrm{VO(dmso)_3(dmso^*)(dmso)_{ax}}]^{2+}\cdots\mathrm{DMSO}$$

$$\xrightarrow[\text{fast}]{} [\mathrm{VO(dmso)_3(dmso^*)(dmso)_{ax}}]^{2+} + \mathrm{DMSO},$$

where an asterisk is used to denote the exchanging species, $(\mathrm{dmso})_{ax}$ represents the coordinated dmso to the axial site, K_{os} is the formation constant of the outer-sphere complex, $[\mathrm{VO(dmso)_4(dmso)_{ax}}]^{2+}\cdots\mathrm{DMSO}^*$, and k_I is the dmso interchange rate constant between the dmso molecules in the equatorial sites and those in the second-coordination sphere above the triangular faces of the octahedral $[\mathrm{VO(dmso)_5}]^{2+}$ ion[7,16] or the rate constant for a process involving intramolecular rearrangement of the coordinated dmso from the axial to the equatorial sites in $[\mathrm{VO(dmso)_4(dmso)_{ax}}]^{2+}$.[17,18] For this mechanism, k_{ex} is given by

$$k_{ex} = k_\mathrm{I}K_{os}[\mathrm{DMSO}]/(1+K_{os}[\mathrm{DMSO}]). \qquad (5)$$

If $K_{os}[\mathrm{DMSO}] \gg 1$, Eq. 5 can be simplified as $k_{ex}=k_\mathrm{I}$ and gives the independence of the exchange rate from the DMSO concentration. In the present study, it is suggested that DMSO molecules may preferentially solvate around the $[\mathrm{VO(dmso)_5}]^{2+}$ ion from the spectrophotometric results. This preferential solvation is due to the fact that the basity of DMSO is larger than that of $\mathrm{CD_3NO_2}$ on the basis of Gutmann's donor number (DN).[19] In a previous paper[20] dealing with the dmso exchange of $\mathrm{UO_2(acac)_2dmso}$ in $\mathrm{CD_2Cl_2}$, the K_{os} value for the formation of $\mathrm{UO_2(acac)_2dmso}\cdots\mathrm{DMSO}$ was found to be *ca.* $5\,\mathrm{M^{-1}}(\mathrm{M{=}mol\,dm^{-3}})$. The K_{os} value for the present study is expected to be larger than $5\,\mathrm{M^{-1}}$ in spite of the fact that the dielectric constant of $\mathrm{CD_3NO_2}$(35.94) is larger than that of $\mathrm{CD_2Cl_2}$(8.93), because the positively charged $[\mathrm{VO(dmso)_5}]^{2+}$ ion has a stronger affinity for DMSO than does the neutral $\mathrm{UO_2(acac)_2dmso}$ complex. Therefore, it seems reasonable to consider that the condition, $K_{os}[\mathrm{DMSO}] \gg 1$, is satisfied in the present study, and that the dmso exchange proceeds through the I mechanism. Especially, the $\mathrm{I_a}$ mechanism seems more likely because of the negative $\Delta V^{\neq}$ value. Nishizawa and Saito have proposed that the rate constant for the intramolecular rearrangement from the axial to the equatorial site is $\simeq 10^3\,\mathrm{s^{-1}}$ at 25 °C. Since this value is comparable to the value for $k_{ex}(1.8\times10^3\,\mathrm{s^{-1}}$ at 25 °C) in our study, the possibility exists that the k_I pathway might be the intramolecular rearrangement proposed by Nishizawa and Saito.

The kinetic parameters for the present and previous studies on the ligand-exchange reactions in oxovanadium(IV) complexes are summarized in Table 2. For the ligand-exchange reactions in oxovanadium(IV) complexes with the ligands coordinated through oxygen, the values of exchange rate constants are almost identical with each other within a factor of 23, and the differences in $\Delta H^{\neq}$ value are also small in spite of the large differences in basicity and size of ligands. These facts suggest that the ligand-exchange reactions in oxovanadium(IV) complexes may not proceed dissociatively because the ligand basicity is one of the dominant kinetic factors in the dissociative process. On the other hand, Caldin and Bennetto proposed that the substitution reactions proceeding dissociatively exhibit an isokinetic relationship between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values.[15] Figure 2 shows the plot of $\Delta H^{\neq}$ *vs.* $\Delta S^{\neq}$ for the ligand exchange reactions in the equatorial site of oxovanadium(IV) complexes and reveals that the isokinetic

TABLE 2. KINETIC PARAMETERS FOR LIGAND EXCHANGE REACTIONS IN $[\mathrm{VO(L)_5}]^{2+}$

L[a]	k_{ex}(25 °C)[b] / $\mathrm{s^{-1}}$	$\Delta H^{\neq}$ / $\mathrm{kJ\,mol^{-1}}$	$\Delta S^{\neq}$ / $\mathrm{J\,K^{-1}\,mol^{-1}}$	Ref.
$\mathrm{H_2O}$	7.4×10^2 (eq)	55.6	−6.3	1
	$\sim10^{11}$ (ax)			1
	5.0×10^2 (eq)	57.3	−2.4	2
$\mathrm{CH_3OH}$	3.3×10^2 (eq)	50.4	−5.5	3
$\mathrm{CH_3CN}$	2.9×10^3 (eq)	29.6	−84	3
dmf	2.0×10^2 (eq)	54.8± 2.5	−17.2± 7.5	4
	4.6×10^4 (ax)	64.0±10.5	58.2±37.7	4
dma	4.7×10^3 (eq)	42.3± 2.1	−33.1± 6.7	4
dmso	1.8×10^3 (eq)	60.1± 4.3	18.5±12.9	This work

a) dmf = *N,N*-dimethylformamide, and dma = *N,N*-dimethylacetamide. b) (eq) and (ax) denote the ligand exchange reactions in the equatorial and axial sites in $[\mathrm{VO(L)_5}]^{2+}$, respectively.

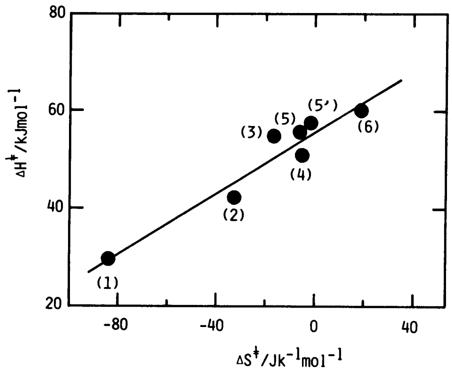

Fig. 2. A plot of ΔH^{*} vs. ΔS^{*} for the ligand exchange reactions in $[VO(L)_5]^{2+}$. L=CH_3CN (1), dma (2), dmf (3), CH_3OH (4), H_2O (5 and 5′), and dmso (6).

relationship is satisfied. Hence, if the proposal by Caldin and Bennetto is acceptable, the possibility still remains, in which the ligand-exchange reactions in oxovanadium(IV) complexes proceed dissociatively. Further studies for the activation volume and anation reactions in oxovanadium(IV) complexes are necessary to clarify the mechanism of the ligand exchange in the present complex.

References

1) J. Reuben and D. Fiat, *Inorg. Chem.*, **6**, 579 (1967).

2) K. Wuthrich and R. E. Connick, *Inorg. Chem.*, **6**, 583 (1967).

3) N. S. Angerman and R. B. Jordan, *Inorg. Chem.*, **8**, 65, (1969).

4) G. A. Miller and R. E. D. McClung, *J. Chem. Phys.*, **58**, 4358 (1969).

5) S. F. Lincoln, *Pure Appl. Chem.*, **51**, 2059 (1979).

6) H. Tomiyasu, S. Ito, and S. Tagami, *Bull. Chem. Soc. Jpn.*, **47**, 2843 (1974).

7) H. Tomiyasu and G. Gordon, *Inorg. Chem.*, **15**, 870 (1976).

8) O. Yokoyama, H. Tomiyasu, and G. Gordon, *Inorg. Chem.*, **21**, 1136 (1982).

9) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).

10) M. Harada, Y. Ikeda, H. Tomiyasu, and H. Fukutomi, *Chem. Lett.* **1984**, 1195.

11) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

12) L. Rusnak and R. B. Jordan, *Inorg. Chem.*, **11**, 196 (1972).

13) D. R. Stranks, *Pure Appl. Chem.*, **38**, 303 (1974).

14) F. K. Meyer, K. E. Newman, and A. E. Merbach, *J. Am. Chem. Soc.*, **101**, 5588 (1979).

15) E. F. Caldin and H. P. Bennetto, *J. Soln. Chem.*, **2**, 217 (1973).

16) K. Wuthrich and R. E. Connick, *Inorg. Chem.*, **7**, 1377 (1968).

17) M. Nishizawa and K. Saito, *Inorg. Chem.*, **17**, 3676 (1978).

18) M. Nishizawa and K. Saito, *Inorg. Chem.*, **19**, 2284 (1980).

19) V. Gutmann and R. Schmid, *Coord. Chem. Rev.*, **12**, 263 (1974).

20) Y. Ikeda, H. Tomiyasu, and H. Fukutomi, *Bull. Chem. Soc. Jpn.*, **56**, 1060 (1983).